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### (54) Metal complex compounds, process for preparation and method of use

Metallkomplex-Verbindungen, Verfahren zur Herstellung und Verfahren zur Verwendung

Composés complexes de métal, leur procédé de préparation et leur procédé d'utilisation

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(60) Divisional application: 96119151.7

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**Description**

This invention relates to compositions of matter which are useful as catalysts, to a method for preparing these catalysts and to a method of using these catalysts for polymerizing addition polymerizable monomers.

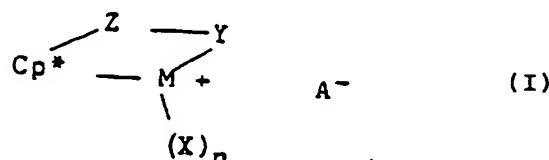
In EP-A-0277004 there are disclosed certain bis(cyclopentadienyl) metal compounds formed by reacting a bis(cyclopentadienyl) metal complex with salts of Bronsted acids containing a noncoordinating compatible anion. The reference discloses the fact that such complexes are usefully employed as catalysts in the polymerization of olefins.

Despite the utility of the catalysts disclosed in the above prior art references it is desirable to produce even more efficient and useful catalysts for addition polymerizations. In particular the present investigations have led to certain improved metal complex containing compounds that are highly active as polymerization catalysts and desirably allow for the polymerization of a wide variety of monomers and mixtures of monomers.

According to the present invention there is now provided a monocyclopentadienyl or substituted monocyclopentadienyl metal complex containing compound corresponding to the formula I:

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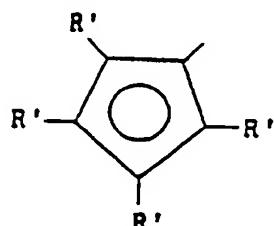


25 wherein:

$\text{Cp}^*$  is a single  $\eta^5$ -cyclopentadienyl or  $\eta^5$ -substituted cyclopentadienyl group optionally covalently bonded to M through -Z-Y- and corresponding to the formula:

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wherein R' each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R' groups together form a fused ring system;

45 M is a metal selected from hafnium, zirconium and titanium bound in an  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group;

X is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof (e.g. haloalkyl, haloaryl, halosilyl, alkaryl, aralkyl, silylalkyl, aryloxyaryl, and alkyoxyalkyl, amidoalkyl, amidoaryl) having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

50 n is 1;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally

Z and Y together form a fused ring system; and

A⁻ is a noncoordinating, compatible anion of a Bronsted acid salt.

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Such compounds are usefully employed in coordination type polymerization processes to prepare polymers for molding, film, sheet, extrusion foaming and other applications. The compounds may also be utilized in hydrogenation reactions, catalytic cracking and other industrial processes.

The compounds of the present invention can be prepared by combining:

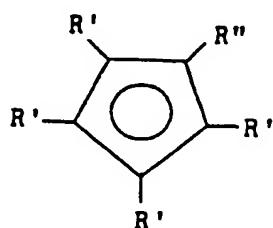
a) at least one first component which is a mono(cyclopentadienyl) derivative of a metal of Group 3-10 or the Lanthanide Series of the Periodic Table of the Elements containing at least one substituent which will combine with the cation of a second component (described hereinafter) which first component is capable of forming a cation formally having a coordination number that is one less than its valence,  
 b) and at least one second component which is a salt of a Bronsted acid and a noncoordinating, compatible anion in an inert, aprotic solvent and recovering, if desired, the resulting product.

More particularly the noncoordinating, compatible anion of the Bronsted acid salt may comprise a single coordination complex comprising a charge-bearing metal or metalloid core, which anion is both bulky and non-nucleophilic. The recitation "metalloid", as used herein, includes non-metals such as boron and phosphorus which exhibit semi-metallic characteristics.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

As used herein, the recitation "noncoordinating, compatible anion" means an anion which either does not coordinate to the monocyclopentadienyl or substituted monocyclopentadienyl group containing cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating, compatible anion specifically refers to a compatible anion which when functioning as a charge balancing anion in the catalyst system of this invention does not transfer an anionic substituent or fragment thereof to said cation thereby forming a neutral four coordinate metallocene and a neutral metal byproduct. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

Monocyclopentadienyl and substituted monocyclopentadienyl groups for use according to the present invention are depicted by the formula:

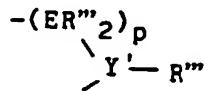


wherein:

R' each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R' groups together form a fused ring system; and

R" is a group that is covalently bonded to M of the formula: -Z-Y-, wherein Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; and Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system.

In a highly preferred embodiment R" is



wherein:

- E each occurrence is carbon, silicon, or germanium;
- 5 p is an integer from 1 to 4;
- Y' is nitrogen or phosphorous; and
- R'' each occurrence is alkyl, aryl, silyl or a combination thereof (e.g. alkaryl, aralkyl, silylalkyl, etc.) having up to 10 carbon or silicon atoms.

Highly preferred compositions according to the invention correspond to the formula I wherein:

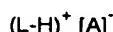
- 10 Z is SiR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>, SiR<sup>\*</sup><sub>2</sub>SiR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>CR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup>=CR<sup>\*</sup>, CR<sup>\*</sup><sub>2</sub>SiR<sup>\*</sup><sub>2</sub>, or GeR<sup>\*</sup><sub>2</sub>;
- Y is a nitrogen or phosphorus containing group corresponding to the formula -N(R''')- or -P(R''')-; wherein:
- R\* each occurrence is hydrogen or a moiety selected from alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups and combinations thereof having up to 20 non-hydrogen atoms,
- 15 R''' is C<sub>1-10</sub> alkyl or C<sub>6-10</sub> aryl, or two or more R\* groups or one or more R\* groups and R''' together form a fused ring system of up to 30 non-hydrogen atoms; and
- X is halo, alkyl, aryl, alkoxy, or aryloxy of up to 20 carbons.

The monocyclopentadienyl metal components (first components) which may be used in the preparation of the compounds of this invention are derivatives of titanium, zirconium or hafnium. Preferred components are titanium or zirconium compounds. Examples of suitable monocyclopentadienyl metal compounds are (tert-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (tert-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) methylenetitanium dichloride, (tert-butylamido)dibenzyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanezirconium dibenzyl, (benzylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanezirconium dichloride, and (phenylphosphido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanezirconium dibenzyl.

Such components are readily prepared by combining the corresponding metal chloride with a dilithium salt of the substituted cyclopentadienyl group such as a cyclopentadienyl-alkanediyl, cyclopentadienyl-silane amide, or cyclopentadienyl-phosphide compound. The reaction is conducted in an inert liquid such as tetrahydrofuran, C<sub>5-10</sub> alkanes, and toluene utilizing conventional synthetic procedures.

Compounds useful as a second component in the preparation of the compounds of this invention will comprise a cation, which is a Bronsted acid capable of donating a proton, and a compatible noncoordinating anion. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 3-10 or Lanthanide Series cation) which is formed when the two components are combined and said anion will be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers and nitriles. Suitable metals include, but are not limited to, aluminum, gold, and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially. In light of this, salts containing anions comprising a coordination complex containing a single boron atom are preferred.

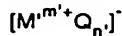
Preferably the second component useful in the preparation of the catalysts of this invention may be represented by the following general formula:



wherein:

- 50 L is a neutral Lewis base;
- (L-H)<sup>+</sup> is a Bronsted acid; and
- A<sup>-</sup> is a compatible, noncoordinating anion.

55 More preferably A<sup>-</sup> corresponds to the formula:



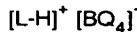
wherein:

$m'$  is an integer from 1 to 7;

$n'$  is an integer from 2 to 8;

5  $M'$  is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements; and  
 Q each occurrence is hydride or a moiety selected from dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide.

10 Second components comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



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wherein:

L is a neutral Lewis base;

[L-H]<sup>+</sup> is a Brønsted acid;

20 B is boron in a valence state of 3; and

Q is as previously defined.

Illustrative, but not limiting, examples of boron compounds which may be used as a second component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such as triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, trimethylammonium tetra(p-tolylborate), tributylammonium tetrakis-pentafluorophenylborate, tripropylammonium tetrakis-2,4-dimethylphenylborate, tributylammonium tetrakis-3,5-dimethylphenylborate, and triethylammonium tetrakis-(3,5-di-trifluoromethylphenyl)borate. Also suitable are N,N-dialkyl anilinium salts such as N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, and N,N-2,4,6-pentamethylanilinium tetraphenylborate; dialkyl ammonium salts such as di-(i-propyl)ammonium tetrakis-pentafluorophenylborate and dicyclohexylammonium tetraphenylborate; and triaryl phosphonium salts such as triphenylphosphonium tetraphenylborate, and tri(methylphenyl)phosphonium tetrakis-pentafluorophenylborate, tri(dimethylphenyl)phosphonium tetraphenylborate.

It should be noted that the foregoing list is not intended to be exhaustive and other boron compounds that would be useful as well as useful components containing other metals or metalloids will be readily apparent from the foregoing general formula and examples to those skilled in the art.

In general, and while most first components identified above may be combined with most second components identified above to produce an active olefin polymerization catalyst, it is important to continued polymerization operations that either the metal cation initially formed from the first component or a decomposition product thereof be a relatively stable catalyst. It is also important that the anion of the second compound be stable to hydrolysis when an ammonium salt is used. Further, it is important that the acidity of the second component be sufficient, relative to the first, to facilitate the needed proton transfer. Conversely, the basicity of the metal complex must also be sufficient to facilitate the needed proton transfer. Certain metallocene compounds are resistant to reaction with all but the strongest Brønsted acids and thus are not suitable as first components to form the catalysts of this invention with all second components. Most preferred monocyclopentadienyl metal compounds are those which can be hydrolyzed by aqueous solutions.

With respect to the combination of first (metal containing) component to second component to form a catalyst of this invention, it should be noted that the two components that are combined for preparation of the active catalyst must be selected so as to avoid transfer of a fragment of the anion, particularly an aryl group, or a fluorine or hydrogen atom to the metal cation, thereby forming a catalytically inactive species. This could be done by steric hindrance, resulting from substitutions on the cyclopentadienyl carbon atoms as well as substitutions on the aromatic carbon atoms of the anion. It follows that first components comprising perhydrocarbyl-substituted cyclopentadienyl radicals could be effectively used with a broader range of second compounds than could first components comprising unsubstituted cyclopentadienyl radicals. As the amount and size of the substitutions on the cyclopentadienyl radicals are reduced, however, more effective catalysts are obtained with second compounds containing anions which are more resistant to degradation, such as those with substituents on the ortho positions of the phenyl rings. Another means of rendering the anion more resistant to degradation is afforded by fluorine substitution, especially perfluoro-substitution, in the anion. Fluoro-substituted stabilizing anions may, then, be used with a broader range of first components.

In general, the catalyst can be prepared by combining the two components in a suitable solvent at a temperature

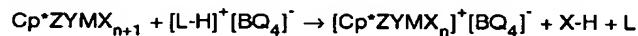
within the range from -100°C to 300°C. The catalyst may be used to polymerize  $\alpha$ -olefins and/or acetylenically unsaturated monomers having from 2 to 18 carbon atoms and/or diolefins having from 4 to 18 carbon atoms either alone or in combination. The catalyst may also be used to polymerize  $\alpha$ -olefins, diolefins and/or acetylenically unsaturated monomers in combination with other unsaturated monomers. In a preferred embodiment the catalysts are employed  
 5 to prepare copolymers of mixtures of vinyl aromatic monomers with olefins other than a vinyl aromatic monomer, specifically copolymers of styrene with ethylene or propylene. In general, the polymerization may be accomplished at conditions well known in the prior art. It will, of course, be appreciated that the catalyst system will form in situ if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the catalyst in a separate  
 10 step in a suitable solvent prior to adding the same to the polymerization step. While the catalysts may not contain pyrophoric species, the catalysts' components are sensitive to both moisture and oxygen and should be handled and transferred in an inert atmosphere such as nitrogen, argon or helium.

As indicated supra, the improved catalyst of the present invention will, preferably, be prepared in a suitable inert, aprotic solvent or diluent. Suitable solvents or diluents include any of the solvents known in the prior art to be useful  
 15 as solvents in the polymerization of olefins, diolefins and acetylenically unsaturated monomers. Suitable solvents include, but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, and octane; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, and methylcycloheptane and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, and xylenes. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene,  
 20 propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, and styrene.

While the inventors do not wish to be bound by any particular theory, it is believed that when the two components used to prepare the improved catalysts of the present invention are combined in a suitable solvent or diluent, all or part of the cation of the second component (the acidic proton) combines with one of the substituents (X) on the first component. As a result a neutral compound, XH is liberated, which neutral compound either remains in solution or is liberated as a gas. In this regard, it should be noted that if X in the first component is hydride, hydrogen gas may be liberated. Similarly, if X is a methyl radical, methane may be liberated as a gas. If X is alkoxide an alcohol results, etc.

While still not wishing to be bound by any particular theory, it is also believed that as one of the first component substituents is liberated, the noncoordinating anion originally contained in the second component used in the catalyst preparation balances the charge of either the metal cation formed from the first component, or a decomposition product thereof. The metal cation and noncoordinating anion will remain so combined until the catalyst is contacted with one or more olefins, diolefins and/or acetylenically unsaturated monomers either alone or in combination with one or more other monomers or another neutral Lewis base. As indicated supra, the anion contained in the second compound must be sufficiently labile to permit rapid displacement by a monomer to facilitate polymerization.

The chemical reactions which occur in forming the catalysts of this invention may, when a preferred, boron containing compound is used as the second component, be represented by reference to the general formula set forth herein as follows:



wherein Cp\*, M, X, Z, Y, n and Q have the previously identified meanings.

In general the stability and rate of formation of the products in the foregoing reaction equations, particularly the metal cation, will vary depending upon the choice of the solvent, the acidity of the [L-H]<sup>+</sup> selected, the particular L, the anion, the temperature at which the reaction is completed and the particular monocyclopentadienyl derivative of the metal selected. Generally, the initially formed ion-pair will be an active polymerization catalyst and will polymerize  $\alpha$ -olefins, diolefins and acetylenically unsaturated monomers either alone or in combination with other monomers. In some cases, however, the initial metal cation will decompose to yield an active polymerization catalyst.

As indicated supra, most first compounds identified above will combine with most second compounds identified above to produce an active catalyst, particularly an active polymerization catalyst. The actual active catalyst species is not, however, always sufficiently stable as to permit its separation and subsequent identification. Moreover, and while many of the initial metal cations formed are relatively stable, it has become apparent that the initially formed metal cation frequently decomposes into one or more other catalytically active species.

In general, catalysts according to the present invention can be selected so as to produce polymer products that will be free of certain trace metals generally found in polymers produced with Ziegler-Natta type catalysts containing cocatalysts such as aluminum or magnesium based compounds. The polymer products produced with the catalyst of this invention should have a broader range of applications than polymers produced with more conventional Ziegler-Natta type catalysts comprising a metal alkyl, such as an aluminum alkyl, or an aluminoxane. The catalysts may be

employed as homogeneous catalysts or supported on the surface of a suitable support such as alumina or silica.

In a preferred embodiment, the catalyst is used to polymerize one or more C<sub>2</sub>-C<sub>8</sub> α-olefins particularly ethylene or propylene, most preferably ethylene, at a temperature within the range from 0°C to 200°C, preferably 25°C to 100°C and at a pressure within the range from atmospheric to 1000 psig (7 MPa) preferably 15 to 500 psig (0.1 - 3.5 MPa).

5 In a most preferred embodiment of the present invention, the catalyst will be used either to homopolymerize ethylene or to copolymerize ethylene with a C<sub>3</sub>-C<sub>8</sub> α-olefin (including styrene) thereby yielding an copolymer. In both the preferred and most preferred embodiments, the monomers will be maintained at polymerization conditions for a nominal holding time within the range from 1 to 60 minutes and the catalyst will be used at a concentration within the range from 10<sup>-7</sup> to 10<sup>-1</sup> moles per mole of monomer.

10 Having thus broadly described the present invention it is believed that the same will become even more apparent by reference to the following examples. It will be appreciated, however, that the examples are presented solely for the purpose of illustration and should not be construed as limiting the invention.

#### Example 1

15 (Tert-butylamido)dimethyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl)silanetitaniumdimethyl and triethylenamoniumtetrakis(pentafluorophenyl) borate

20 A 25 mL flask was charged with 275 mg of (tert-butylamido)(dimethyl)(η<sup>5</sup>-tetramethylcyclopentadienyl)silanetitanium dichloride, 0.75 mmol) and attached to a small frit. The frit was evacuated and 15 mL of diethyl ether was vacuum transferred into the flask. At -78°C, 1.1 mL of MeLi (1.4 M in hexane, 1.54 mmol, 2.05 equiv) was added through the sidearm valve using a syringe. No color change was noted. After 5 minutes, the bath was removed and the solution allowed to warm to room temperature. After 1 h. the solution was dark green and opaque. The diethyl ether was stripped off and replaced with 10 mL of hexane. The solution was stirred at 25°C for 10 min and then filtered. The solid was reduced to about 2 mL, the solution cooled to -78°C, and the frit cold-flipped to collect a dark olive solid. After drying under reduced pressure for 30 min, the solid (tert-butylamido)dimethyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl)silanetitanium dimethyl was isolated (138 mg, 56 percent).

#### Polymerization

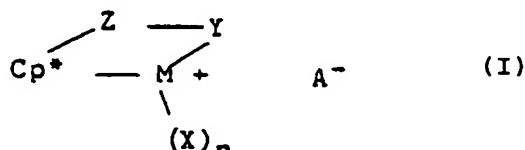
30 A 100 mL three-neck flask was charged with 32 mg (98 μmol) of (tert-butylamido)dimethyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl)silanetitanium dimethyl. The flask was equipped with a stopper, vacuum line adapter, and a solids addition funnel. The addition funnel was charged with 77 mg of [HNEt<sub>3</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> and stoppered. The flask was evacuated and 50 mL of benzene was distilled onto the solid. The solution was warmed to 25°C and blanketed with 1 atm. (0.1 MPa) of ethylene. The solid [HNEt<sub>3</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> was then added resulting in a yellow solution. After one hour, the viscous, yellow solution was still taking up ethylene. The resulting gelatinous mixture was quenched with methanol to give a white precipitate. The material was filtered, washed twice with methanol, and dried in a vacuum over to give 0.56 g of polyethylene.

40

#### Claims

45 Claims for the following Contracting States : BE, DE, FR, GB, IT, NL, SE

1. A monocyclopentadienyl or substituted monocyclopentadienyl metal complex containing compound corresponding to the formula I:

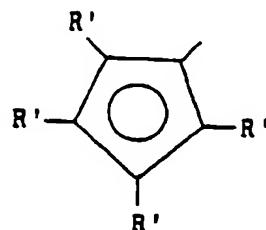


wherein:

Cp\* is a single  $\eta^5$ -cyclopentadienyl or  $\eta^5$ -substituted cyclopentadienyl group covalently bonded to M through -Z-Y- and corresponding to the formula:

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10



15

wherein:

R' each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R' groups together form a fused ring system;

M is a metal selected from hafnium, zirconium and titanium bound in an  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group;

X is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

n is 1;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

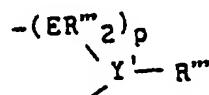
Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system; and

A<sup>-</sup> is a noncoordinating, compatible anion of a Bronsted acid salt.

2. A compound as claimed in Claim 1, wherein X is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof having up to 20 non-hydrogen atoms.

40 3. A compound as claimed in Claim 1 or Claim 2, wherein -Z-Y- is:

45



50 wherein:

E each occurrence is carbon, silicon, or germanium;

p is an integer from 1 to 4;

55 Y' is nitrogen or phosphorous; and

R'' each occurrence is alkyl, aryl, silyl or a combination thereof having up to 10 carbon or silicon atoms.

4. A compound as claimed in any one of the preceding claims, wherein M is titanium or zirconium.

5. A compound as claimed in Claim 4, wherein:

5 Z is  $\text{SiR}^*_2$ ,  $\text{CR}^*_2$ ,  $\text{SiR}^*_2\text{SiR}^*_2$ ,  $\text{CR}^*_2\text{CR}^*_2$ ,  $\text{CR}^*=\text{CR}^*$ ,  $\text{CR}^*_2\text{SiR}^*_2$ , or  $\text{GeR}^*_2$ ;

10 Y is a nitrogen or phosphorus containing group corresponding to the formula  $-\text{N}(\text{R}^{**})-$  or  $-\text{P}(\text{R}^{**})-$ ; wherein:

R\* each occurrence is hydrogen or a moiety selected from alkyl, aryl, silyl, halogenated alkyl, halogenated aryl groups and combinations thereof having up to 20 non-hydrogen atoms,

15 R\*\* is  $\text{C}_{1-10}$  alkyl or  $\text{C}_{6-10}$  aryl, or two or more R\* groups or one or more R\* groups and R\*\* together form a fused ring system of up to 30 non-hydrogen atoms;

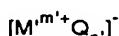
X is a moiety selected from halo, alkyl, aryl, alkoxy, and aryloxy of up to 20 carbons.

6. A compound as claimed in any one of the preceding claims, wherein X is  $\text{C}_{1-4}$  alkyl or alkoxy.

20 7. A compound as claimed in Claim 5, wherein X is methyl.

8. A compound as claimed in Claim 5, wherein X is benzyl.

9. A compound as claimed in any one of the preceding claims, wherein A<sup>-</sup> corresponds to the formula:



wherein:

30 m' is an integer from 1 to 7;

n' is an integer from 2 to 8;

35 M' is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements; and

Q each occurrence is hydride or a moiety selected from dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide.

40 10. A compound as claimed in Claim 9, wherein A<sup>-</sup> corresponds to the formula:



45 wherein B is boron in a valence state of 3 and Q is as defined in Claim 9.

11. A compound as claimed in any one of the preceding claims, wherein A<sup>-</sup> is a fluoro-substituted anion.

50 12. A compound as claimed in any one of the preceding claims, wherein A is tetrakis-pentafluorophenyl borate.

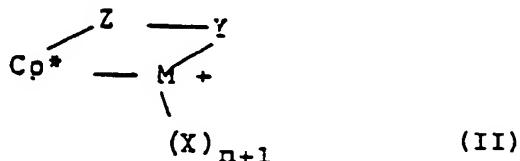
55 13. A compound as claimed in Claim 1, which is derived from (tert-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (tert-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-methylenetitanium dichloride, (tert-butylamido)dibenzyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane-zirconium dibenzyl, (benzylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanezirconium dichloride, and (phenylphosphido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane-zirconium dibenzyl.

14. A compound as claimed in Claim 1, wherein A<sup>-</sup> is derived from triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, trimethylammonium tetra(p-tolylborate), tributylammonium tetrakis-pentafluorophenylborate, tripropylammonium tetrakis-2,4-dimethylphenylborate, tributylammonium tetrakis-3,5-dimethylphenylborate, triethylammonium tetrakis-(3,5-di-trifluoromethylphenyl)borate, N, N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-2,4,6-pentamethylanilinium tetraphenylborate, di-(i-propyl)ammonium tetrakis-pentafluorophenylborate, dicyclohexylammonium tetraphenylborate, triphenylphosphonium tetraphenylborate, tri(methylphenyl)phosphonium tetrakis-pentafluorophenylborate, and tri(dimethylphenyl)phosphonium tetraphenylborate.

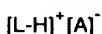
15. A compound as claimed in Claim 1, wherein Cp\* is perhydrocarbyl-substituted.

16. (Tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane titanium methyl tetrakis-pentafluorophenylborate.

17. A process for preparing a compound as claimed in Claim 1 comprising contacting a first component corresponding to the formula II



30 wherein Cp\*, M, X, Z, Y and n are as defined in Claim 1  
with a second component corresponding to the formula



35 wherein L is a neutral Lewis base and A<sup>-</sup> is as defined in Claim 1  
in an inert, aprotic solvent.

18. A process as claimed in Claim 17, wherein Cp\*, M, X, Y, Z, n and A<sup>-</sup> are as defined in any one of Claims 2 to 16.

40 19. The use of a compound as claimed in any one of Claims 1 to 16 as an addition polymerization catalyst.

20. An addition polymerization process for preparing a polymer by contacting one or more addition polymerizable monomers with a coordination polymerization catalyst under addition polymerization conditions, characterized in that the catalyst is a compound as defined in any one of Claims 1 to 16.

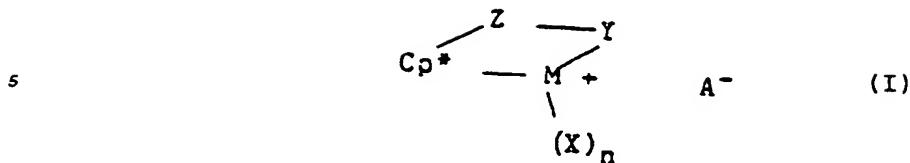
45 21. A process as claimed in Claim 20, wherein ethylene is homopolymerized or copolymerized with a C<sub>3</sub>-C<sub>8</sub> alpha-olefin.

22. A process as claimed in Claim 21, wherein ethylene is copolymerized with styrene.

50 23. A process as claimed in any one of Claims 20 to 22, wherein the catalyst is formed *in situ*.

Claims for the following Contracting State : ES

55 1. A process for preparing a monocyclopentadienyl or substituted monocyclopentadienyl metal complex containing compound corresponding to the formula I:



wherein:

15 Cp\* is a single  $\eta^5$ -cyclopentadienyl or  $\eta^5$ -substituted cyclopentadienyl group covalently bonded to M through -Z-Y- and corresponding to the formula:



wherein:

30 R' each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R' groups together form a fused ring system;

35 M is a metal selected from hafnium, zirconium and titanium bound in an  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group;

40 40 R' each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

n is 1;

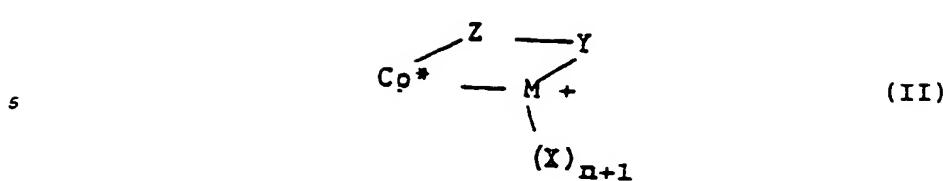
Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements;

45 Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system; and

A<sup>-</sup> is a noncoordinating, compatible anion of a Brønsted acid salt,

50 comprising contacting a first component corresponding to the formula II

55



10 wherein Cp\*, M, X, Z, Y and n are as defined above,  
 with a second component corresponding to the formula  $[\text{L}-\text{H}]^+[\text{A}]^-$ , wherein L is a neutral Lewis base and A is as  
 defined above, in an inert, aprotic solvent.

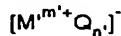
15 2. A process as claimed in Claim 1, wherein X is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl,  
 aryloxy, alkoxy, amide, siloxy, and combinations thereof having up to 20 non-hydrogen atoms.  
 3. A process as claimed in Claim 1 or Claim 2, wherein -Z-Y- is:



25 wherein:  
 E each occurrence is carbon, silicon, or germanium; p is an integer from 1 to 4;  
 Y' is nitrogen or phosphorous; and

30 R'' each occurrence is alkyl, aryl, silyl or a combination thereof having up to 10 carbon or silicon atoms.

4. A process as claimed in any one of the preceding claims, wherein M is titanium or zirconium.  
 35 5. A process as claimed in Claim 4, wherein:  
 Z is  $\text{SiR}^*_2$ ,  $\text{CR}^*_2$ ,  $\text{SiR}^*_2\text{SiR}^*_2$ ,  $\text{CR}^*_2\text{CR}^*_2$ ,  $\text{CR}^*=\text{CR}^*$ ,  $\text{CR}^*_2\text{SiR}^*_2$ , or  $\text{GeR}^*_2$ ;  
 Y is a nitrogen or phosphorus containing group corresponding to the formula  $-\text{N}(\text{R}'')-$  or  $-\text{P}(\text{R}'')-$ ; wherein:  
 40 R\* each occurrence is hydrogen or a moiety selected from alkyl, aryl, silyl, halogenated alkyl, halogenated  
 aryl groups and combinations thereof having up to 20 non-hydrogen atoms,  
 R'' is C<sub>1-10</sub> alkyl or C<sub>6-10</sub> aryl, or two or more R\* groups or one or more R\* groups and R'' together form a  
 fused ring system of up to 30 non-hydrogen atoms; and  
 X is a moiety selected from halo, alkyl, aryl, alkoxy, and aryloxy of up to 20 carbons.  
 45 6. A process as claimed in any one of the preceding claims, wherein X is C<sub>1-4</sub> alkyl or alkoxy.  
 7. A process as claimed in Claim 5, wherein X is methyl.  
 50 8. A process as claimed in Claim 5, wherein X is benzyl.  
 9. A process as claimed in any one of the preceding claims, wherein A<sup>-</sup> corresponds to the formula:



55 wherein:  
 m' is an integer from 1 to 7;

n' is an integer from 2 to 8;

M' is a metal or metalloid selected from Groups 5-15 of the Periodic Table of the Elements; and Q each occurrence is hydride or a moiety selected from dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, and substituted-hydrocarbyl radicals of up to 20 carbons with the proviso that in not more than one occurrence is Q halide.

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10. A process as claimed in Claim 9, wherein A<sup>-</sup> corresponds to the formula:



wherein:

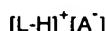
B is boron in a valence state of 3 and Q is as defined in Claim 9.

15. 11. A process as claimed in any one of the preceding claims, wherein A<sup>-</sup> is a fluoro-substituted anion.

12. A process as claimed in any one of the preceding claims, wherein A is tetrakis-pentafluorophenyl borate.

20. 13. A process as claimed in Claim 1, wherein the compound of formula II is (tert-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (tert-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (methylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediylzirconium dichloride, (methylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride, (ethylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl)-methylene titanium dichloride, (tert-butylamido)dibenzyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane zirconium dibenzyl, (benzylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl) silane titanium dichloride, and (phenylphosphido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl) silane zirconium dibenzyl.

25. 14. A process as claimed in Claim 1, wherein the compound of formula

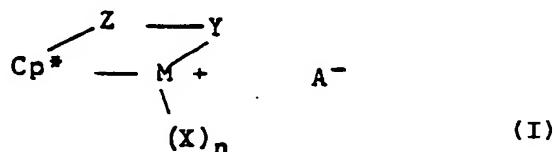


30. is triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, trimethylammonium tetra(p-tolylborate), tributylammonium tetrakis-pentafluorophenylborate, tripropylammonium tetrakis-2,4-dimethylphenylborate, tributylammonium tetrakis-3,5-dimethylphenylborate, triethylammonium tetrakis-(3,5-di-trifluoromethylphenyl)borate, N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-2,4,6-pentamethylanilinium tetraphenylborate, di-(i-propyl)ammonium tetrakis-pentafluorophenylborate, dicyclohexylammonium tetraphenylborate, triphenylphosphonium tetraphenylborate, tri(methylphenyl)phosphonium tetrakis-pentafluorophenylborate, and tri(dimethylphenyl)phosphonium tetraphenylborate.

35. 40. 15. A process as claimed in Claim 1, wherein Cp\* is perhydrocarbyl-substituted.

16. A process as claimed in Claim 1, wherein (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane titanium dimethyl is reacted with triethyleneammonium tetrakis-pentafluorophenylborate.

45. 17. The use as an addition polymerization catalyst of a monocyclopentadienyl or substituted monocyclopentadienyl metal complex containing compound corresponding to the formula I:



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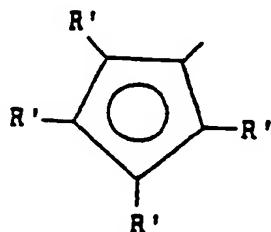
wherein:

Cp\* is a single  $\eta^5$ -cyclopentadienyl or  $\eta^5$ -substituted cyclopentadienyl group covalently bonded to M through -Z-Y-and corresponding to the formula:

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15



wherein:

R' each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof of up to 20 non-hydrogen atoms, or two or more R' groups together form a fused ring system;

M is a metal selected from hafnium, zirconium and titanium bound in an  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group;

X is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

n is 1;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system; and

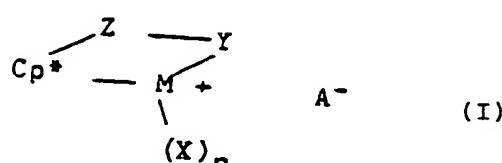
A<sup>-</sup> is a noncoordinating, compatible anion of a Bronsted acid salt.

18. A use as claimed in Claim 17, wherein Cp\*, M, X, Z, Y, n and A<sup>-</sup> are as defined in any one of Claims 2 to 16.

35 19. An addition polymerization process for preparing a polymer by contacting one or more addition polymerizable monomers with a coordination polymerization catalyst under addition polymerization conditions, characterized in that the catalyst is a monocyclopentadienyl or substituted monocyclopentadienyl metal complex containing compound corresponding to the formula I:

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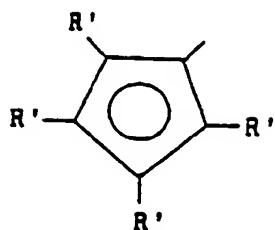
50 wherein:

Cp\* is a single  $\eta^5$ -cyclopentadienyl or  $\eta^5$ -substituted cyclopentadienyl group covalently bonded to M through -Z-Y-and corresponding to the formula:

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wherein:

R' each occurrence is hydrogen or a moiety selected from halogen, alkyl, aryl, haloalkyl, alkoxy, aryloxy, silyl groups, and combinations thereof up to 20 non-hydrogen atoms, or two or more R' groups together form a fused ring system;

M is a metal selected from hafnium, zirconium and titanium bound in an  $\eta^5$  bonding mode to the cyclopentadienyl or substituted cyclopentadienyl group;

X is hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy, and combinations thereof having up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms;

n is 1;

Z is a divalent moiety comprising oxygen, boron, or a member of Group 14 of the Periodic Table of the Elements; Y is a linking group covalently bonded to the metal comprising nitrogen, phosphorus, oxygen or sulfur, or optionally Z and Y together form a fused ring system; and

A<sup>-</sup> is a noncoordinating, compatible anion of a Brønsted acid salt.

20. A process as claimed in Claim 19, wherein Cp\*, M, X, Z, Y, n and A<sup>-</sup> are as defined in any one of Claims 2 to 16.

30. 21. A process as claimed in Claim 19 or Claim 20, wherein ethylene is homopolymerized or copolymerized with a C<sub>3</sub>-C<sub>8</sub> alpha-olefin.

22. A process as claimed in Claim 21, wherein ethylene is copolymerized with styrene.

35. 23. A process as claimed in any one of Claims 21 to 22, wherein the catalyst is formed *in situ*.

#### Patentansprüche

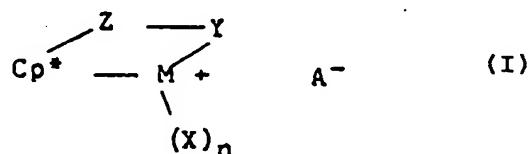
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Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, IT, NL, SE

1. Monocyclopentadienyl- oder substituierter Monocyclopentadienylmetallkomplex, enthaltend eine Verbindung entsprechend der Formel I:

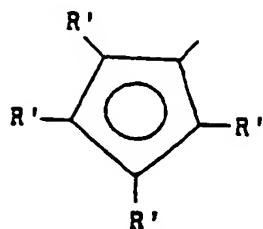
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in der CP\* eine einzelne  $\eta^5$ -Cyclopentadienyl- oder  $\eta^5$ -substituierte Cyclopentadienylgruppe ist, die kovalent an M über -Z-Y- gebunden ist und der Formel



entspricht, in der

15 R' bei jedem Auftreten Wasserstoff oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Halogenalkyl, Alkoxy, Aryloxy, Silylgruppen und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen ist, oder zwei oder mehrere R'-Gruppen zusammen ein kondensiertes Ringsystem ausbilden,

M ein Metall, ausgewählt aus Hafnium, Zirkonium und Titan, ist, das über eine  $\eta^5$ -Bindung an die Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe gebunden ist,

20 X Hydrid oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Silyl, Germyl, Acryloxy, Alkoxy, Amid, Siloxy und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen und neutralen Lewis-Baseliganden mit bis zu 20 Nichtwasserstoffatomen, ist,

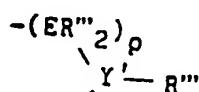
n = 1 ist,

Z eine divalente Gruppe umfassend Sauerstoff, Bor oder ein Mitglied der Gruppe 14 des Periodensystems der Elemente ist,

25 Y eine verknüpfende Gruppe, die kovalent an das Metall gebunden ist, umfassend Stickstoff, Phosphor, Sauerstoff oder Schwefel ist oder wahlweise Z und Y zusammen ein kondensiertes Ringsystem bilden und A ein nichtkoordinierendes kompatibles Anion eines Brönsted-Säuresalzes ist.

30 2. Verbindung nach Anspruch 1, worin X Hydrid oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Silyl, Germyl, Aryloxy, Alkoxy, Amid, Siloxy und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen, ist.

35 3. Verbindung nach Anspruch 1 oder 2, worin -Z-Y-



ist, in der

45 E bei jedem Auftreten Kohlenstoff, Silicium oder Germanium ist,

p eine ganze Zahl von 1-4 ist,

Y' Stickstoff oder Phosphor ist und

R'' bei jedem Auftreten Alkyl, Aryl, Silyl oder eine Kombination daraus mit bis zu 10 Kohlenstoff- oder Siliciumatomen ist.

50 4. Verbindung nach einem der vorstehenden Ansprüche, worin M Titan oder Zirconium ist.

55 5. Verbindung nach Anspruch 4, worin

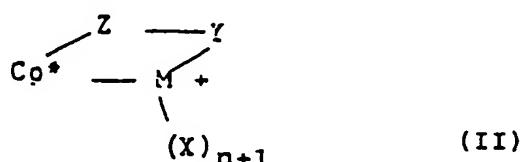
Z SiR\*<sub>2</sub>, CR\*<sub>2</sub>, SiR\*<sub>2</sub>SiR\*<sub>2</sub>, CR\*<sub>2</sub>CR\*<sub>2</sub>, CR\*=CR\*, CR\*<sub>2</sub>SiR\*<sub>2</sub> oder GeR\* ist,

Y eine stickstoff- oder phosphorhaltige Gruppe entsprechend der Formel -N(R'')- oder -P(R'')- ist, in der R'' bei jedem Auftreten Wasserstoff oder eine Gruppe ausgewählt aus Alkyl, Aryl, Silyl, halogeniertem Alkyl, halogenierten Arylgruppen und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen ist,

R'' C<sub>1-10</sub>-Alkyl oder C<sub>6-10</sub>-Aryl ist oder zwei oder mehrere R\*-Gruppen oder eine oder mehrere R\*-Gruppen

und R<sup>m</sup> zusammen ein kondensiertes Ringsystem mit bis zu 30 Nichtwasserstoffatomen bilden und X eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Alkoxy und Aryloxy mit bis zu 20 Kohlenstoffatomen, ist.

6. Verbindung nach einem der vorstehenden Ansprüche, worin X C<sub>1-4</sub>-Alkyl oder -Alkoxy ist.  
 5  
 7. Verbindung nach Anspruch 5, worin X Methyl ist.  
 8. Verbindung nach Anspruch 5, worin X Benzyl ist.  
 10 9. Verbindung nach einem der vorstehenden Ansprüche, worin  
 A<sup>-</sup> der Formel [M<sup>m'+</sup>Q<sub>n'</sub>]<sup>-</sup> entspricht, in der  
 m' eine ganze Zahl von 1-7 ist,  
 n' eine ganze Zahl von 2-8 ist,  
 15 M' ein Metall oder Metalloid ausgewählt aus den Gruppen 5-15 des Periodensystems der Elemente ist und  
 Q bei jedem Auftreten Hydrid oder eine Gruppe ausgewählt aus Dialkylamido, Halogenid, Alkoxid, Aryloxid,  
 Kohlenwasserstoff- und substituierten Kohlenwasserstoffresten mit bis zu 20 Kohlenstoffatomen ist unter der  
 Voraussetzung, daß Q bei nicht mehr als einem Auftreten Halogenid ist.  
 20 10. Verbindung nach Anspruch 9, worin A<sup>-</sup> der Formel [BQ<sub>4</sub>]<sup>-</sup> entspricht, in der  
 B Bor im Valenzzustand 3 ist und Q wie in Anspruch 9 definiert ist.  
 11. Verbindung nach einem der vorstehenden Ansprüche, worin A<sup>-</sup> ein fluorsubstituiertes Anion ist.  
 25 12. Verbindung nach einem der vorstehenden Ansprüche, worin A Tetrakis(pentafluorphenyl)borat ist.  
 13. Verbindung nach Anspruch 1, worin die Verbindung der Formel II (tert-Butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethandiylzirconiumdichlorid, (tert-Butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethandiyltitandichlorid, (Methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethandiylzirconiumdichlorid, (Methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethandiyltitandichlorid, (Ethylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-methylentitandichlorid, (tert-Butylamido)dibenzyl(tetramethyl- $\eta^5$ -cyclopentadienyl) silanzirconiumdibenzyl, (Benzylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silantitan dichlorid oder (Phenylphosphido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanzirconiumdibenzyl ist.  
 30 35 14. Verbindung nach Anspruch 1, worin die Verbindung der Formel [L-H]<sup>+</sup>[A<sup>-</sup>] Triethylammonium-tetraphenylborat, Tripropylammonium-tetraphenylborat, Tripropylammonium-tetraphenylborat, Tri(n-butyl)ammonium-tetraphenylborat, Trimethylammonium-tetra(p-tolylborat), Tributylammonium-tetrakis(pentafluorophenyl)borat, Tripropylammonium-tetrakis(2,4-dimethylphenyl)borat, Tributylammonium-tetrakis(3,5-dimethylphenyl)borat, Triethylammonium-tetrakis-(3,5-di-trifluormethylphenyl)borat, N,N-Dimethylanilinium-tetraphenylborat, N,N-Diethylanilinium-tetraphenylborat, N,N-2,4,6-Pentamethylanilinium-tetraphenylborat, Di(i-propyl)ammonium-tetrakis(pentafluorophenyl)borat, Dicyclohexylammonium-tetraphenylborat, Triphenylphosphonium-tetraphenylborat, Tri(methylphenyl)phosphonium-tetrakis(pentafluorophenyl)borat oder Tri(dimethylphenyl)phosphonium-tetraphenylborat.  
 40 45 15. Verbindung nach Anspruch 1, worin Cp<sup>\*</sup> perhydrocarbylsubstituiert ist.  
 16. (tert-Butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silantitanmethyltetrakis(pentafluorophenyl)borat.  
 17. Verfahren zur Herstellung einer Verbindung nach Anspruch 1 umfassend Inkontaktbringen einer ersten Komponente entsprechend der Formel II  
 50



in der CP\*, M, X, Z, Y und n wie oben definiert sind,  
mit einer zweiten Komponente entsprechend der Formel [L-H]<sup>+</sup>[A], in der L eine neutrale Lewis-Base und A wie  
in Anspruch 1 definiert ist,  
in einem inerten aprotischen Lösungsmittel.

5            18. Verfahren nach Anspruch 17, worin Cp\*, M, X, Z, Y, n und A<sup>-</sup> wie in einem der Ansprüche 2-16 definiert sind.

10          19. Verwendung einer Verbindung nach einem der Ansprüche 1-16 als Additionspolymerisationskatalysator.

15          20. Additionspolymerisationsverfahren zur Herstellung eines Polymers durch Inberührungbringen eines oder mehrerer  
additionspolymerisierbarer Monomere mit einem Koordinationspolymerisationskatalysator unter Additionspolymerisationsbedingungen,  
dadurch gekennzeichnet,  
daß der Katalysator eine Verbindung wie in einem der Ansprüche 1-16 definiert ist.

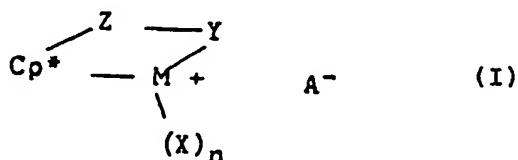
20          21. Verfahren nach Anspruch 20, worin Ethylen homopolymerisiert oder mit einem C<sub>3</sub>-C<sub>8</sub>-alpha-Olefin copolymerisiert  
wird.

25          22. Verfahren nach Anspruch 21, worin Ethylen mit Styrol copolymerisiert wird.

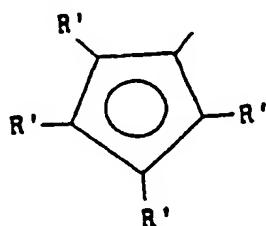
30          23. Verfahren nach einem der Ansprüche 20-22, worin der Katalysator in situ gebildet wird.

Patentansprüche für folgenden Vertragsstaat : ES

25          1. Verfahren zur Herstellung eines Monocyclopentadienyl- oder substituierten Monocyclopentadienylmetall-  
komplexes, enthaltend eine Verbindung entsprechend der Formel I:



40          40        in der CP\* eine einzelne  $\eta^5$ -Cyclopentadienyl- oder  $\eta^5$ -substituierte Cyclopentadienylgruppe ist, die kovalent an  
M über -Z-Y- gebunden ist und der Formel



entspricht, in der

55          55        R' bei jedem Auftreten Wasserstoff oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Halogenalkyl,  
Alkoxy, Aryloxy, Silylgruppen und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen ist, oder zwei  
oder mehrere R'-Gruppen zusammen ein kondensiertes Ringsystem ausbilden,  
M ein Metall, ausgewählt aus Hafnium, Zirkonium und Titan, ist, das über eine  $\eta^5$ -Bindung an die Cyclopentadienylgruppe gebunden ist.

tadienyl- oder substituierte Cyclopentadienylgruppe gebunden ist,  
 X Hydrid oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Silyl, Germyl, Acryloxy, Alkoxy, Amid, Siloxy und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen und neutralen Lewis-Baseliganden mit bis zu 20 Nichtwasserstoffatomen ist,

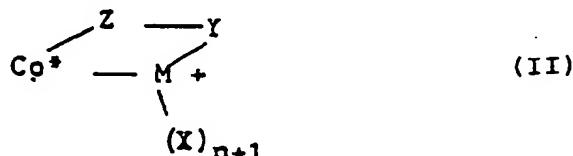
5 n = 1 ist,

Z eine divalente Gruppe umfassend Sauerstoff, Bor oder ein Mitglied der Gruppe 14 des Periodensystems der Elemente ist,

10 Y eine verknüpfende Gruppe, die kovalent an das Metall gebunden ist, umfassend Stickstoff, Phosphor, Sauerstoff oder Schwefel ist oder wahlweise Z und Y zusammen ein kondensiertes Ringsystem bilden und A ein nichtkoordinierendes kompatibles Anion eines Brönsted-Säuresalzes ist,

wobei das Verfahren umfaßt: Inkontaktbringen einer ersten Komponente entsprechend der Formel II

15



20

in der CP\*, M, X, Z, Y und n wie oben definiert sind,  
 25 mit einer zweiten Komponente entsprechend der Formel [L-H]<sup>+</sup>[A]<sup>-</sup>, in der L eine neutrale Lewis-Base und A wie oben definiert ist, in einem inerten aprotischen Lösungsmittel.

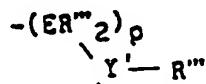
25

2. Verfahren nach Anspruch 1, worin worin X Hydrid oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Silyl, Germyl, Aryloxy, Alkoxy, Amid, Siloxy und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen, ist.

30

3. Verfahren nach Anspruch 1 oder 2, worin -Z-Y-

35



40 ist, in der

40

E bei jedem Auftreten Kohlenstoff, Silicium oder Germanium ist,

p eine ganze Zahl von 1-4 ist,

Y' Stickstoff oder Phosphor ist und

45

R'' bei jedem Auftreten Alkyl, Aryl, Silyl oder eine Kombination daraus mit bis zu 10 Kohlenstoff- oder Siliciumatomen ist.

45

4. Verfahren nach einem der vorstehenden Ansprüche, worin M Titan oder Zirconium ist.

50

5. Verfahren nach Anspruch 4, worin

50

Z SiR''<sub>2</sub>, CR''<sub>2</sub>, SiR''<sub>2</sub>SiR''<sub>2</sub>, CR''<sub>2</sub>CR''<sub>2</sub>, CR''=CR'', CR''<sub>2</sub>SiR''<sub>2</sub> oder GeR'' ist,

Y eine stickstoff- oder phosphorhaltige Gruppe entsprechend der Formel -N(R'')- oder -P(R'')- ist, in der R'' bei jedem Auftreten Wasserstoff oder eine Gruppe ausgewählt aus Alkyl, Aryl, Silyl, halogeniertem Alkyl, halogenierten Arylgruppen und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen ist,

55

R'' C<sub>1-10</sub>-Alkyl oder C<sub>6-10</sub>-Aryl ist oder zwei oder mehrere R''-Gruppen oder eine oder mehrere R''-Gruppen und R''' zusammen ein kondensiertes Ringsystem mit bis zu 30 Nichtwasserstoffatomen bilden und X eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Alkoxy und Aryloxy mit bis zu 20 Kohlenstoffatomen, ist.

6. Verfahren nach einem der vorstehenden Ansprüche, worin X C<sub>1-4</sub>-Alkyl oder -Alkoxy ist.

7. Verfahren nach Anspruch 5, worin X Methyl ist.

5 8. Verfahren nach Anspruch 5, worin X Benzyl ist.

9. Verfahren nach einem der vorstehenden Ansprüche, worin

10 A<sup>-</sup> der Formel [M<sup>m'+</sup>Q<sub>n</sub>]<sup>-</sup> entspricht, in der  
m' eine ganze Zahl von 1-7 ist,  
n' eine ganze Zahl von 2-8 ist,  
M' ein Metall oder Metalloid ausgewählt aus den Gruppen 5-15 des Periodensystems der Elemente ist und  
Q bei jedem Auftreten Hydrid oder eine Gruppe ausgewählt aus Dialkylamido, Halogenid, Alkoxid, Aryloxid,  
Kohlenwasserstoff- und substituierten Kohlenwasserstoffresten mit bis zu 20 Kohlenstoffatomen ist unter der  
Voraussetzung, daß Q bei nicht mehr als einem Auftreten Halogenid ist.

15 10. Verfahren nach Anspruch 9, worin A<sup>-</sup> der Formel [BQ<sub>4</sub>]<sup>-</sup> entspricht, in der  
B Bor im Valenzzustand 3 ist und Q wie in Anspruch 9 definiert ist.

20 11. Verfahren nach einem der vorstehenden Ansprüche, worin A<sup>-</sup> ein fluorsubstituiertes Anion ist.

12. Verfahren nach einem der vorstehenden Ansprüche, worin A Tetrakis(pentafluorphenyl)borat ist.

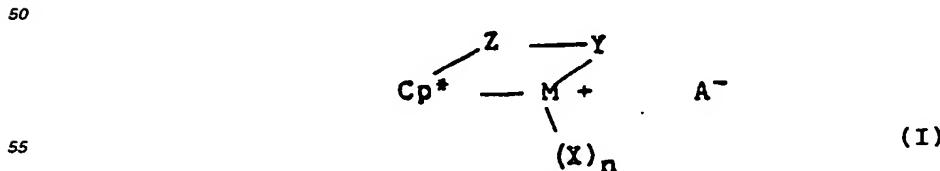
25 13. Verfahren nach Anspruch 1, worin die Verbindung der Formel II (tert-Butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)-1,2-ethandiylzirconiumdichlorid, (tert-Butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)-1,2-ethandiyltitandichlorid, (Methylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)-1,2-ethandiylzirconiumdichlorid, (Methylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)-1,2-ethandiyltitandichlorid, (Ethylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)-methylentitandichlorid, (tert-Butylamido)dibenzyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl) silanzirconiumdibenzyl, (Benzylamido)dime-thyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl)silantitandichlorid oder (Phenylphosphido)dimethyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl)silanzirconiumdibenzyl ist.

30 14. Verfahren nach Anspruch 1, worin die Verbindung der Formel [L-H]<sup>+</sup>[A<sup>-</sup>] Triethylammonium-tetraphenylborat, Tri-propylammonium-tetraphenylborat, Tripropylammonium-tetraphenylborat, Tri(n-butyl)ammonium-tetraphenylborat, Trimethylammonium-tetra(p-tolylborat), Tributylammonium-tetrakis(pentafluorophenyl)borat, Tripropylammonium-tetrakis-2,4-dimethylphenylborat, Tributylammonium-tetrakis-3,5-dimethylphenylborat, Triethylammonium-tetrakis-(3,5-di-trifluormethylphenyl)borat, N,N-Dimethylanilinium-tetraphenylborat, N,N-Diethylanilinium-tetraphenylborat, N,N-2,4,6-Pentamethylanilinium-tetraphenylborat, Di(i-propyl)ammonium-tetrakis(pentafluorophenyl)borat, Dicyclohexylammonium-tetraphenylborat, Triphenylphosphonium-tetraphenylborat, Tri(methylphenyl)phosphonium-tetrakis(pentafluorophenyl)borat oder Tri(dimethylphenyl)phosphonium-tetraphenylborat.

40 15. Verfahren nach Anspruch 1, worin Cp\* perhydrocarbylsubstituiert ist.

16. Verfahren nach Anspruch 1, worin (tert-Butylamido)dimethyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl)silantitandimethyl mit Triethylammonium-tetrakis(pentafluorophenyl)borat umgesetzt wird.

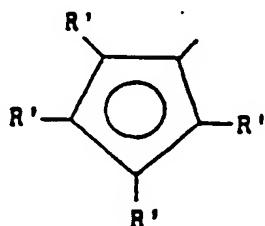
45 17. Verwendung eines Additionspolymerisationskatalysators aus einem Monocyclopentadienyl- oder substituiertem Monocyclopentadienylmetallkomplex, der eine Verbindung entsprechend der Formel I



enthält,  
in der CP\* eine einzelne  $\eta^5$ -Cyclopentadienyl oder  $\eta^5$ -substituierte Cyclopentadienylgruppe ist, die kovalent an M über -Z-Y- gebunden ist und der Formel

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15

entspricht, in der

R' bei jedem Auftreten Wasserstoff oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Halogenalkyl, Alkoxy, Aryloxy, Silylgruppen und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen ist, oder zwei oder mehrere R'-Gruppen zusammen ein kondensiertes Ringsystem ausbilden,

20 M ein Metall, ausgewählt aus Hafnium, Zirkonium und Titan, ist, das über eine  $\eta^5$ -Bindung an die Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe gebunden ist,

X Hydrid oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Silyl, Germyl, Acryloxy, Alkoxy, Amid, Siloxy und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen und neutralen Lewis-Baseliganden mit bis

25 zu 20 Nichtwasserstoffatomen, ist,

$n = 1$  ist,

Z eine divalente Gruppe umfassend Sauerstoff, Bor oder ein Mitglied der Gruppe 14 des Periodensystems der Elemente ist,

30 Y eine verknüpfende Gruppe, die kovalent an das Metall gebunden ist, umfassend Stickstoff, Phosphor, Sauerstoff oder Schwefel ist oder wahlweise Z und Y zusammen ein kondensiertes Ringsystem bilden und A<sup>-</sup> ein nichtkoordinierendes kompatibles Anion eines Brönsted-Säuresalzes ist.

18. Verwendung nach Anspruch 17, worin Cp\*, M, X, Z, Y, n und A<sup>-</sup> wie in einem der Ansprüche 2-16 definiert sind.

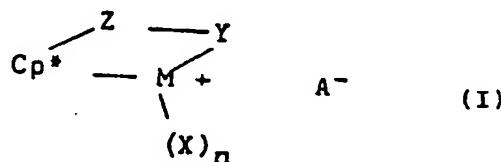
35 19. Additionspolymerisationsverfahren zur Herstellung eines Polymers durch Inberührungsbringen eines oder mehrerer additionspolymerisierbarer Monomere mit einem Koordinationspolymerisationskatalysator unter Additionspolymerisationsbedingungen,

dadurch gekennzeichnet,

40 daß der Katalysator ein Monocyclopentadienyl- oder substituierter Monocyclopentadienylmetallkomplex ist, der eine Verbindung entsprechend der Formel I enthält:

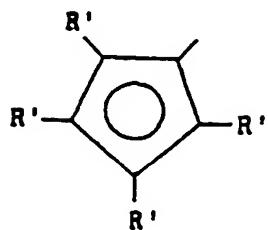
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in der CP\* eine einzelne  $\eta^5$ -Cyclopentadienyl oder  $\eta^5$ -substituierte Cyclopentadienylgruppe ist, die kovalent an M über -Z-Y- gebunden ist und der Formel

55



entspricht, in der

R' bei jedem Auftreten Wasserstoff oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Halogenalkyl, Alkoxy, Aryloxy, Silylgruppen und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen ist, oder zwei oder mehrere R'-Gruppen zusammen ein kondensiertes Ringsystem ausbilden,  
 M ein Metall, ausgewählt aus Hafnium, Zirkonium und Titan, ist, das über einer  $\eta^5$ -Bindung an die Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe gebunden ist,  
 X Hydrid oder eine Gruppe, ausgewählt aus Halogen, Alkyl, Aryl, Silyl, Germyl, Acryloxy, Alkoxy, Amid, Siloxy und Kombinationen daraus mit bis zu 20 Nichtwasserstoffatomen und neutralen Lewis-Baseliganden mit bis zu 20 Nichtwasserstoffatomen ist,  
 n = 1 ist,  
 Z eine divalente Gruppe umfassend Sauerstoff, Bor oder ein Mitglied der Gruppe 14 des Periodensystems der Elemente ist,  
 Y eine verknüpfende Gruppe, die kovalent an das Metall gebunden ist, umfassend Stickstoff, Phosphor, Sauerstoff oder Schwefel ist oder wahlweise Z und Y zusammen ein kondensiertes Ringsystem bilden und  
 A' ein nichtkoordinierendes kompatibles Anion eines Brönsted-Säuresalzes ist.

**20. Verfahren nach Anspruch 19, worin Cp\*, M, X, Z, Y, n und A wie in einem der Ansprüche 2-16 definiert sind.**

21. Verfahren nach Anspruch 19 oder 20, worin Ethylen homopolymerisiert oder mit einem C<sub>3</sub>-C<sub>8</sub>-alpha-Olefin copolymerisiert wird.

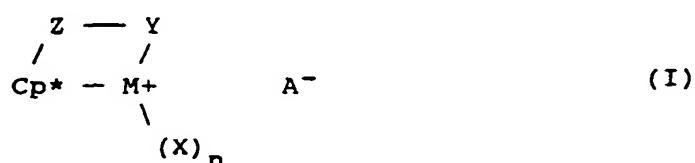
22. Verfahren nach Anspruch 21, worin Ethylen mit Styrol copolymerisiert wird.

**23. Verfahren nach Anspruch 21 oder 22, worin der Katalysator *in situ* gebildet wird.**

### **Reverendations**

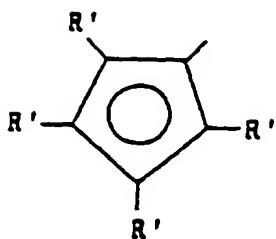
#### **Revendications pour les Etats contractants suivants : BE, DE, FR, GB, IT, NL, SE**

1. Composé contenant un complexe métallique de monocyclopentadiényle ou de monocyclopentadiényle substitué correspondant à la formule I:



**dans laquelle:**

$Cp^*$  est un groupe  $\eta^5$ -cyclopentadiényle ou  $\eta^5$ -cyclopentadiénide substitué unique lié par covalence à M par l'intermédiaire de -Z-Y- et correspondant à la formule:



dans laquelle:

15 chaque R' représente un hydrogène ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, halogénoalkyle, alcoxy, aryloxy, silyle et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, ou deux ou plusieurs groupes R' forment ensemble un système cyclique condensé;

M est un métal choisi parmi le hafnium, le zirconium et le titane, lié par une liaison de type  $\eta^5$  au groupe cyclopentadiényle ou cyclopentadiényle substitué;

20 X est un hydrure ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, silyle, germyle, aryloxy, alcoxy, amide, siloxy et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, et les ligands de base de Lewis neutre ayant jusqu'à 20 atomes différents de l'hydrogène;

n vaut 1;

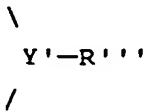
25 Z est un groupe divalent comprenant de l'oxygène, du bore, ou un élément du Groupe 14 du Tableau Périodique des Éléments;

Y est un groupe de liaison lié par covalence au métal, comprenant de l'azote, du phosphore, de l'oxygène ou du soufre, ou éventuellement Z et Y forment ensemble un système cyclique condensé; et

A<sup>-</sup> est un anion compatible de non coordination d'un sel d'acide de Bronsted.

30 2. Composé selon la revendication 1, dans lequel X est un hydrure ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, silyle, germyle, aryloxy, alkoxy, amide, siloxy et leurs combinaisons comportant jusqu'à 20 atomes différents de l'hydrogène.

35 3. Composé selon l'une des revendications 1 ou 2, dans lequel  
-Z-Y- est:



45

chaque E est un carbone, un silicium ou un germanium;

p est un nombre entier de 1 à 4;

Y' est l'azote ou le phosphore; et

50 chaque R'' est un groupe alkyle, aryle, silyle, ou une de leurs combinaisons ayant jusqu'à 20 atomes de carbone ou de silicium.

4. Composé selon l'une des revendications précédentes, dans lequel M est le titane ou le zirconium.

55 5. Composé selon la revendication 4, dans lequel:

Z est SiR''<sub>2</sub>, CR''<sub>2</sub>, SiR''<sub>2</sub>SiR''<sub>2</sub>, CR''<sub>2</sub>CR''<sub>2</sub>, CR''=CR'', CR''<sub>2</sub>SiR''<sub>2</sub>, ou GeR''<sub>2</sub>;

Y est un groupe contenant de l'azote ou du phosphore correspondant à la formule -N(R'')- ou -P(R''')-; dans

lesquels:

chaque R\* est un hydrogène ou un radical choisi parmi les groupes alkyle, aryle, silyle, alkylhalogéné, arylhalogéné et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène,

R\*\* représente un groupe alkyle en C<sub>1</sub> à C<sub>10</sub> ou aryle en C<sub>6</sub> à C<sub>10</sub>, ou bien deux ou plusieurs groupes R\* ou bien un ou plusieurs groupes R\* et R\*\* forment ensemble un système cyclique condensé ayant jusqu'à 30 atomes différents de l'hydrogène;

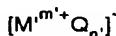
X est un radical choisi parmi les radicaux halogéno, alkyle, aryle, alcoxy, et aryloxy ayant jusqu'à 20 atomes de carbone.

6. Composé selon l'une des revendications précédentes, dans lequel X est un groupe alkyle ou alcoxy en C<sub>1</sub> à C<sub>4</sub>.

7. Composé selon la revendication 5, dans lequel X est un groupe méthyle.

8. Composé selon la revendication 5, dans lequel X est un groupe benzyle.

9. Composé selon l'une des revendications précédentes, dans lequel A<sup>-</sup> correspond à la formule:



dans laquelle:

m' est un nombre entier de 1 à 7;

n' est un nombre entier de 2 à 8;

M' est un métal ou un métalloïde choisi parmi les groupes 5 à 15 du Tableau Périodique des Eléments; et chaque Q est un hydrure ou un radical choisi parmi les radicaux dialkylamido, halogénure, alcoxyde, aryloxyde, hydrocarbyle, et hydrocarbyle substitué ayant jusqu'à 20 atomes de carbone à condition que pas plus d'un des Q ne soit un halogénure.

10. Composé selon la revendication 9, dans lequel A<sup>-</sup> correspond à la formule:



dans laquelle:

B est un atome de bore dans un état de valence de 3 et Q est tel que défini dans la revendication 9.

11. Composé selon l'une des revendications précédentes, dans lequel A<sup>-</sup> est un anion fluorosubstitué.

12. Composé selon l'une des revendications précédentes, dans lequel A est le borate de tétrakis-pentafluorophényle.

13. Composé selon la revendication 1, qui est dérivé du dichlorure de (t-butylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediylzirconium, du dichlorure de (t-butylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediyltitane, du dichlorure de (méthylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediyl-zirconium, du dichlorure de (méthylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediyltitane, du dichlorure d'(éthylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-méthylènetitanate, du (t-butylamido)dibenzyl(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)silanedibenzyl zirconium, du dichlorure de (benzylamido)diméthyl(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)silanetitanate, et du (phénylphosphido)diméthyl(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)silanedibenzyl zirconium.

14. Composé selon la revendication 1, dans lequel A<sup>-</sup> est dérivé du tétraphénylborate de triéthylammonium, du tétraphénylborate tripropylammonium, du tétraphénylborate de tri(n-butyl)ammonium, du tétra(p-tolylborate) de triméthylammonium, du tétrakis-pentafluorophénylborate de tributylammonium, du tétrakis-2,4-diméthylphénylborate de tripropylammonium, du tétraphénylborate de triéthylammonium, du tétraphénylborate de N,N-diméthylanilinium, du tétraphénylborate de N,N-diéthylanilinium, du tétraphénylborate de N,N-2,4,6-pentaméthylanilinium, du tétraphénylborate de di-(i-propyl)ammonium, du tétraphénylborate de dicyclohexylammonium, du tétraphénylborate de triphénylphosphonium, du tétrakis-pentafluorophénylborate de tri(méthylphényl)phosphonium, et du tétraphénylborate de tri(diméthylphényl)phosphonium.

15. Composé selon la revendication 1, dans lequel Cp\* est substitué par un groupe perhydrocarbyle.

16. Le tétrakis-pentafluorophénylborate de (*t*-butylamido)diméthyl(tétraméthyl- $\eta^5$ -cyclopentadiényl)silanediéthyl titanate.

5 17. Procédé pour la préparation d'un composé selon la revendication 1 consistant à mettre un premier composant correspondant à la formule II



dans laquelle Cp\*, M, X, Z, Y et n sont tels que définis dans la revendication 1 en contact avec un deuxième composant correspondant à la formule



dans laquelle L est une base de Lewis neutre et A est tel que défini dans la revendication 1 dans un solvant inert et aprotique.

25 18. Procédé selon la revendication 17, dans lequel Cp\*, M, X, Y, Z, n et A- sont tels que définis dans l'une des revendications 2 à 16.

19. Utilisation d'un composé selon l'une des revendications 1 à 16 en tant que catalyseur de polymérisation par addition.

30 20. Procédé de polymérisation par addition pour préparer un polymère en mettant en contact un ou plusieurs monomères polymérisables par addition avec un catalyseur de polymérisation comportant une coordination dans des conditions de polymérisation par addition, caractérisé en ce que le catalyseur est un composé tel que défini dans l'une des revendications 1 à 16.

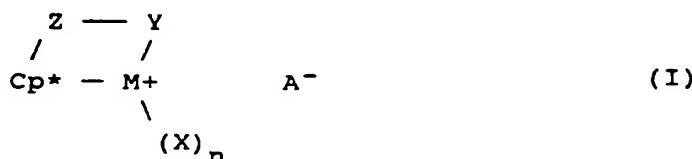
35 21. Procédé selon la revendication 20, dans lequel l'éthylène est homopolymérisé ou copolymérisé avec une alpha-oléfine en C<sub>3</sub> à C<sub>8</sub>.

40 22. Procédé selon la revendication 21, dans lequel l'éthylène est copolymérisé avec le styrène.

23. Procédé selon l'une des revendications 20 à 22, dans lequel le catalyseur est formé in-situ.

45 Revendications pour l'Etat contractant suivant : ES

1. Procédé pour la préparation d'un complexe métallique de monocyclopentadiényle ou de monocyclopentadiényle substitué correspondant à la formule I:



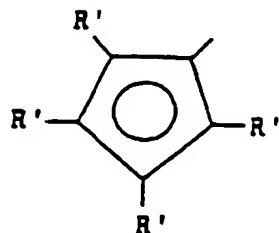
5 dans laquelle:

Cp\* est un groupe  $\eta^5$ -cyclopentadiényle ou  $\eta^5$ -cyclopentadiényle substitué unique lié par covalence à M par l'intermédiaire de -Z-Y- et correspondant à la formule:

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dans laquelle:

20 chaque R' représente un hydrogène ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, halogénoalkyle, alcoxy, aryloxy, silyle et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, ou deux ou plusieurs groupes R' forment ensemble un système cyclique condensé;

M est un métal choisi parmi le hafnium, le zirconium et le titane, lié par une liaison de type  $\eta^5$  au groupe cyclopentadiényle ou cyclopentadiényle substitué;

25 X est un hydrure ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, silyle, germyle, aryloxy, alcoxy, amide, siloxy et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, et les ligands de base de Lewis neutre ayant jusqu'à 20 atomes différents de l'hydrogène;

n vaut 1;

30 Z est un groupe divalent comprenant de l'oxygène, du bore, ou un élément du Groupe 14 du Tableau Périodique des Éléments;

Y est un groupe de liaison lié par covalence au métal, comprenant de l'azote, du phosphore, de l'oxygène ou du soufre, ou éventuellement Z et Y forment ensemble un système cyclique condensé; et

A<sup>-</sup> est un anion compatible de non coordination d'un sel d'acide de Bronsted.

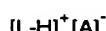
35 consistant à mettre en contact un premier composant correspondant à la formule II

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45 dans laquelle Cp\*, M, X, Z, Y et n sont tels que définis dans la revendication 1 en contact avec un deuxième composant correspondant à la formule

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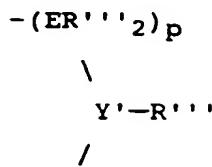
dans laquelle L est une base de Lewis neutre et A est tel que défini dans la revendication 1 dans un solvant inerte et aprotique.

55

2. Procédé selon la revendication 1, dans lequel X est un hydrure ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, silyle, germyle, aryloxy, alkoxy, amide, siloxy et leurs combinaisons comportant jusqu'à 20 atomes différents de l'hydrogène.

3. Procédé selon l'une des revendications 1 ou 2, dans lequel

5 -Z-Y- est:



10

où:

15 chaque E est un carbone, un silicium ou un germanium;  
 p est un nombre entier de 1 à 4;  
 Y' est l'azote ou le phosphore; et  
 chaque R'' est un groupe alkyle, aryle, silyle, ou une de leurs combinaisons ayant jusqu'à 10 atomes de carbone ou de silicium.

20 4. Procédé selon l'une des revendications précédentes, dans lequel M est le titane ou le zirconium.

25 5. Procédé selon la revendication 4, dans lequel:

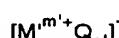
Z est  $\text{SiR}^*_2$ ,  $\text{CR}^*_2$ ,  $\text{SiR}^*_2\text{SiR}^*_2$ ,  $\text{CR}^*_2\text{CR}^*_2$ ,  $\text{CR}^*=\text{CR}^*$ ,  $\text{CR}^*_2\text{SiR}^*_2$ , ou  $\text{GeR}^*_2$ ;  
 30 Y est un groupe contenant de l'azote ou du phosphore correspondant à la formule  $-\text{N}(\text{R}''')$ - ou  $-\text{P}(\text{R}''')$ -; dans lesquels:  
 chaque  $\text{R}^*$  est un hydrogène ou un radical choisi parmi les groupes alkyle, aryle, silyle, alkylhalogéné, aryl-halogéné et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène.  
 R''' représente un groupe alkyle en  $C_1$  à  $C_{10}$  ou aryle en  $C_6$  à  $C_{10}$ , ou bien deux ou plusieurs groupes  $\text{R}^*$  ou bien un ou plusieurs groupes  $\text{R}^*$  et  $\text{R}''''$  forment ensemble un système cyclique condensé ayant jusqu'à 30 atomes différents de l'hydrogène;  
 X est un radical choisi parmi les radicaux halogéno, alkyle, aryle, alcoxy, et aryloxy ayant jusqu'à 20 atomes de carbone.

35 6. Procédé selon l'une des revendications précédentes, dans lequel X est un groupe alkyle ou alcoxy en  $C_1$  à  $C_4$ .

7. Procédé selon la revendication 5, dans lequel X est un groupe méthyle.

8. Procédé selon la revendication 5, dans lequel X est un groupe benzyle.

40 9. Procédé selon l'une des revendications précédentes, dans lequel A<sup>-</sup> correspond à la formule:



45 dans laquelle:

m' est un nombre entier de 1 à 7;  
 n' est un nombre entier de 2 à 8;  
 50 M' est un métal ou un métalloïde choisi parmi les groupes 5 à 15 du Tableau Périodique des Éléments; et chaque Q est un hydrure ou un radical choisi parmi les radicaux dialkylamido, halogénure, alcoxyde, aryloxyde, hydrocarbyle, et hydrocarbyle substitué ayant jusqu'à 20 atomes de carbone à condition que pas plus d'un des Q ne soit un halogénure.

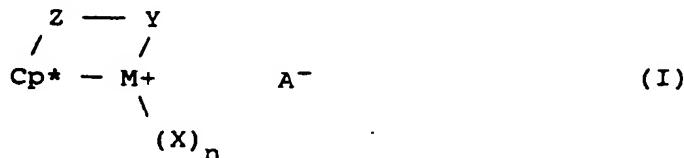
55 10. Procédé selon la revendication 9, dans lequel A<sup>-</sup> correspond à la formule:



dans laquelle:

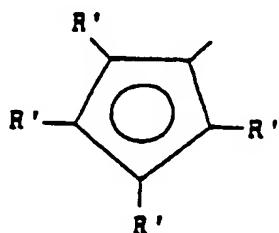
B est un atome de bore dans un état de valence de 3 et Q est tel que défini dans la revendication 9.

- 5 11. Procédé selon l'une des revendications précédentes, dans lequel A<sup>-</sup> est un anion fluorosubstitué.
12. Procédé selon l'une des revendications précédentes, dans lequel A est le borate de tétrakis-pentafluorophényle.
- 10 13. Procédé selon la revendication 1, qui est dérivé du dichlorure de (t-butylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediylzirconium, du dichlorure de (t-butylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediyltitane, du dichlorure de (méthylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediylzirconium, du dichlorure de (méthylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-éthanediyltitane, du dichlorure d'(éthylamido)(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)-1,2-méthylénétitane, du (t-butylamido) dibenzyl(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)silanedi benzyl zirconium, du dichlorure de (benzylamido) diméthyl(tétraméthyl-η<sup>5</sup>-cyclopentadiényl)silanedi benzyl zirconium, et du (phénylphosphido) diméthyl(tétraméthyl-η<sup>5</sup>-cyclopenta-diényl)silanedi benzyl zirconium.
- 15 14. Procédé selon la revendication 1, dans lequel le composé de formule [L-H]<sup>+</sup>[A]<sup>-</sup> est le téraphénylborate de triéthylammonium, du téraphénylborate tripropylammonium, du téraphénylborate de tri(n-butyl)ammonium, du tétra(p-tolylborate) de triméthylammonium, du tétrakis-pentafluorophénylborate de tributylammonium, du tétrakis-2,4-diméthylphénylborate de tripropylammonium, du tétrakis-3,5-diméthylphénylborate de tributylammonium, du tétrakis-(3,5-di-trifluorométhylphényl)borate de triéthylammonium, du téraphénylborate de N,N-diméthylanilinium, du téraphénylborate de N,N-diéthylanilinium, du téraphénylborate de N,N-2,4,6-pentaméthylanilinium, du tétrakis-pentafluorophénylborate de di-(i-propyl)ammonium, du téraphénylborate de dicyclohexylammonium, du téraphénylborate de triphénylphosphonium, du tétrakis-pentafluorophénylborate de tri(méthylphényl)phosphonium, et du téraphénylborate de tri(diméthylphényl)phosphonium.
- 20 15. Procédé selon la revendication 1, dans lequel Cp\* est substitué par un groupe perhydrocarbyle.
- 25 16. Procédé selon la revendication 1, dans lequel on fait réagir le (t-butylamido)diméthyl(tétraméthyl-η<sup>5</sup>-cyclopenta-diényl)silanedi diméthyl titane avec le tétrakispentafluorophényl borate de triéthylammonium.
- 30 17. Utilisation comme catalyseur de polymérisation par addition d'un complexe métallique de monocyclopentadiényle ou de monocyclopentadiényle substitué de formule I



dans laquelle:

Cp\* est un groupe η<sup>5</sup>-cyclopentadiényle ou η<sup>5</sup>-cyclopentadiényle substitué unique lié par covalence à M par l'intermédiaire de -Z-Y- et correspondant à la formule:



dans laquelle:

5 chaque R' représente un hydrogène ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, halogé-noalkyle, alcoxy, aryloxy, silyle et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, ou deux ou plusieurs groupes R' forment ensemble un système cyclique condensé;

M est un métal choisi parmi le hafnium, le zirconium et le titane, lié par une liaison de type  $\eta^5$  au groupe cyclopentadiényle ou cyclopentadiényle substitué;

X est un hydrure ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, silyle, germyle, aryloxy, alcoxy, amide, siloxy et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, et les ligands de base de Lewis neutre ayant jusqu'à 20 atomes différents de l'hydrogène;

n vaut 1;

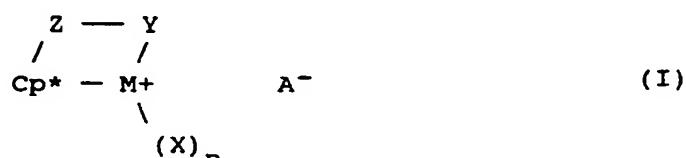
10 Z est un groupe divalent comprenant de l'oxygène, du bore, ou un élément du Groupe 14 du Tableau Périodique des Eléments;

Y est un groupe de liaison lié par covalence au métal, comprenant de l'azote, du phosphore, de l'oxygène ou du soufre, ou éventuellement Z et Y forment ensemble un système cyclique condensé; et

15 A<sup>-</sup> est un anion compatible de non coordination d'un sel d'acide de Bronsted.

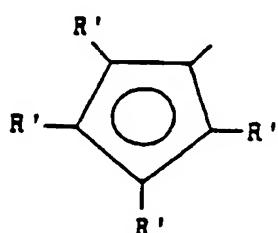
18. Utilisation selon la revendication 17, dans laquelle Cp\*, M, X, Z, Y, n et A<sup>-</sup> sont tels que définis dans l'une des revendications 2 à 16.

19. Procédé de polymérisation par addition pour la préparation d'un polymère en mettant en contact un ou plusieurs monomères polymérisables par addition avec un catalyseur de polymérisation comportant une coordination dans des conditions de polymérisation par addition, caractérisé en ce que le catalyseur est un complexe métallique de monocyclopentadiényle ou de monocyclopentadiényle substitué correspondant à la formule I:



dans laquelle:

35 Cp\* est un groupe  $\eta^5$ -cyclopentadiényle ou  $\eta^6$ -cyclopentadiényle substitué unique lié par covalence à M par l'intermédiaire de -Z-Y- et correspondant à la formule:



dans laquelle:

50 chaque R' représente un hydrogène ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, halogé-noalkyle, alcoxy, aryloxy, silyle et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, ou deux ou plusieurs groupes R' forment ensemble un système cyclique condensé;

55 M est un métal choisi parmi le hafnium, le zirconium et le titane, lié par une liaison de type  $\eta^5$  au groupe cyclopentadiényle ou cyclopentadiényle substitué;

X est un hydrure ou un radical choisi parmi les radicaux halogéno, alkyle, aryle, silyle, germyle, aryloxy, alcoxy, amide, siloxy et leurs combinaisons ayant jusqu'à 20 atomes différents de l'hydrogène, et les ligands de base de Lewis neutre ayant jusqu'à 20 atomes différents de l'hydrogène;

n vaut 1;

Z est un groupe divalent comprenant de l'oxygène, du bore, ou un élément du Groupe 14 du Tableau Périodique des Éléments;

Y est un groupe de liaison lié par covalence au métal, comprenant de l'azot , du phosphore, de l'oxygène ou du soufre, ou éventuellement Z et Y forment ensemble un système cyclique condensé; et A<sup>-</sup> est un anion compatible de non coordination d'un sel d'acide de Bronsted.

5 20. Procédé selon la revendication 19, dans lequel Cp\*, M, X, Z, Y, n et A<sup>-</sup> sont tels que définis dans l'une des revendications 2 à 16.

10 21. Procédé selon l'une des revendications 19 ou 20, dans lequel de l'éthylène est homopolymérisé ou copolymérisé avec une alpha-oléfine en C<sub>3</sub>-C<sub>8</sub>.

15 22. Procédé selon la revendication 21, dans lequel l'éthylène est copolymérisé avec du styrène.

23. Procédé selon l'une des revendications 21 ou 22, dans lequel le catalyseur est formé in situ.

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